



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p><b>(21) International Application Number:</b> PCT/NL98/00544</p> <p><b>(22) International Filing Date:</b> 21 September 1998 (21.09.98)</p> <p><b>(30) Priority Data:</b>          1007086                      19 September 1997 (19.09.97)    NL</p> <p><b>(71) Applicant (for all designated States except US):</b> NORIT MEM-          BRAAN TECHNOLOGIE B.V. [NL/NL]; P.O. Box 89,          NL-7550 AB Hengelo (NL).</p> <p><b>(72) Inventors; and</b>  <b>(75) Inventors/Applicants (for US only):</b> BESEMER, Arie, Cor-          nelis [NL/NL]; Burgemeester Jhr. H. van den Boschstraat          111, NL-3958 CC Amerongen (NL). JETTEN, Jan,          Matthijs [NL/NL]; Costerlaan 3b, NL-3701 JL Zeist (NL).          BROENS, Lute [NL/NL]; Oude Rijssenseweg 18, NL-7475          CN Markelo (NL).</p> <p><b>(74) Agents:</b> DE BRUIJN, Leendert, C. et al.; Nederlandsch          Octrooibureau, Scheveningseweg 82, P.O. Box 29720,          NL-2502 LS The Hague (NL).</p>		<p><b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR,          BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE,          GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ,          LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW,          MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,          TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO          patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian          patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European          patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR,          IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF,          CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b>  <i>With international search report.</i>  <i>In English translation (filed in Dutch).</i></p>
<p><b>(54) Title:</b> PROCESS OF CLEANING FILTERS</p> <p><b>(57) Abstract</b></p> <p>Filters for water purification can be cleaned by treatment with a calcium-binding agent, preferably followed by catalytic oxidation, for example with hypochlorite in the presence of 2,2,6,6-tetra-methylpiperidine-N-oxyl or a similar nitroxyl. The calcium-binding agent is, for example, a dicarboxypolysaccharide, a phosphate or a polyacrylamine. In particular, dicarboxyinulin, optionally in combination with a zeolite, can be used as calcium-binding agent.</p>		

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### Process of cleaning filters

The invention relates to a process of cleaning filters, in particular membrane filters which are used in the purification of surface water.

In the purification of surface water, use is being made to an increasing extent of membrane filters, in particular plastic membranes such as polyvinylpyrrolidone, polysulphone, polyether sulphone and certain types of polyamides. Such membranes ensure an expedient removal of undesirable constituents, in particular microorganisms such as algae, fungi and bacteria. The problem is, however, that the membrane filters become blocked even after a short time so that they become unusable. The blocked filters can be regenerated, for example by rinsing them through in the opposite direction. However, that is a complicated process and no longer effective in the long term because the contamination accumulates. In addition, it is difficult to remove some persistent organic contaminants in this way. It is also known to remove the contaminants oxidatively, for example with permanganate or peroxides, but this is an expensive process and is not always satisfactory in practice.

A process has now been found for oxidatively cleaning filters which can be carried out with relatively cheap agents and has very good efficiency. The process according to the invention is characterised in that the filter is treated with a calcium-binding agent and, preferably, also subjected to catalytic oxidation.

If the pollution of the filters comprises only or essentially organic acids such as humic acid, one treatment with a calcium-binding agent, such as a polydicarboxysaccharide, in particular polydicarboxyinulin, is generally sufficient. If the pollution also contains a large amount of organic material containing primary alcohol functions, such as carbohydrates, a catalytic oxidation is also desirable, preferably at a pH of around 12 (10-12).

The catalytic oxidation can be carried out, for example, with hydrogen peroxide in the presence of a transition metal or a complex thereof, as described in EP-A-733594. A readily usable transition-metal complex is, for example, a complex of a polyamine such as ethylenediamine, diethylenetriamine or, in particular, 1,4,7-triazacyclononane (a cyclic triethylenetriamine) and the N-methylated analogues thereof with a transition metal such as nickel, cobalt or, in particular, iron or

manganese. Optionally, the transition-metal complex can be immobilised, for example by means of a covalent bond at one of the nitrogen atoms, so that the complex is not rinsed away and can easily be used several times.

A still more advantageous oxidation system appears to be an oxidation with  
5 hypochlorite in the presence of a tertiary alkyl nitroxyl compound. Such an oxidation is described, for example, in WO 95/07303. Usable nitroxyl compounds are, for example, di-tertbutylnitroxyl, but reference is made, in particular, to cyclic compounds, such as N-oxylpyrrolidine, -oxazolidine, -piperidine, -piperazine and -morpholine, which are substituted with two alkyl groups on either side of the  
10 nitroxyl group and may furthermore contain additional substitutes such as alkyl, alkoxy, hydroxyl, acyloxy, oxo, halogen, nitro and the like in the ring. Examples thereof are 4,4-dimethyloxazolidine-N-oxyl (DOXYL), 2,2,5,5-tetramethylpyrrolidine-N-oxyl (PROXYL), 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) and the 4-hydroxy-, 4-oxo- and 4-acyloxy- derivatives thereof. TEMPO is preferred  
15 because of its cost price. These compounds may also optionally be bound covalently to a carrier, for example, via the 4-hydroxyl group so that the oxidation catalyst is immobilised at or in the vicinity of the filter to be cleaned. TEMPO is always mentioned in this connection for the sake of simplicity, but the other abovementioned nitroxyl compounds also fall under this designation.

20 The treatment with TEMPO and hypochlorite may be carried out in a manner known per se, for example at room temperature or lower (down to 0°C) and at an elevated pH, for example between 6 and 11. The TEMPO may be present in an amount of 0.1-5% by weight with respect to the contamination present. The hypochlorite will be used in general in a small excess with respect to the  
25 contamination. HOCl is added in portions to protect the membrane against excessively high hypochlorite concentrations. Optionally, to accelerate the oxidation reaction, a small amount of bromide may be present.

The calcium-binding agent can be a compound known as such, for example a phosphate, such as sodium tripolyphosphate (NTPP) or a polyamine, optionally  
30 substituted with alkyl, hydroxyalkyl, acyl or carboxymethyl groups; examples thereof are diethylenetriamine substituted with hydroxyethyl and/or carboxymethyl groups, such as EDTA, nitrilotriacetic acid and the like. Polydicarboxypolysaccharides, such

as polydicarboxystarch, polydicarboxycellulose, polydicarboxypentosans, especially the hydrolysed (shorter-chain) analogues thereof, such as polydicarboxydextrins and, in particular, polydicarboxyinulin (DCI) appear to be particularly suitable as calcium binders. The polydicarboxy(poly)saccharides may have a degree of oxidation of 0.1–1 dicarboxyl group per anhydrofructose unit. Such dicarboxypolysaccharides are disclosed, for example, in EP-A-427349, WO 91/17189 and WO 94/21690. The treatment with the calcium-binding agent may be carried out at room temperature or a lower or higher temperature, and at a usually elevated pH, in particular of 10–12. The calcium-binding agent may also be a silicate or a zeolite, in which case a polydicarboxypolysaccharide may serve as calcium transporter.

The treatment with the calcium-binding agent preferably precedes the oxidation treatment. Advantageously, the calcium-binding agent is combined with a cobuilder, such as a zeolite, which functions as final acceptor of the calcium ions.

## EXAMPLES

### General

The experiments are carried out with a membrane module (where mention is made of a membrane in these examples, said module is always meant). Said module (a tube having a length of 30 cm and a diameter of 2.5 cm) contains 40 hollow fibres, each having a diameter of 1.5 mm; the total effective surface is 0.04 m<sup>2</sup>. The water to be filtered is passed through the fibres. Two possibilities are distinguished for the filtration method:

- the membrane is closed at one end (dead-end filtration),
- is open at one end (cross-flow filtration).

The module is placed in a so-called TRX system. Said system comprises a reservoir (capacity approximately 10 litres), a pump and a facility for measuring the pressure across the filter and keeping it more or less constant. Both dead-end and cross-flow filtering is possible with said system.

In order to assess the effectiveness of the cleaning process, the module is polluted consecutively by filtering surface water with it and then cleaning it by means of one or more treatments using chemicals, after which the degree of cleaning is assessed by comparing the initial clean-water flux (SWF) of a cleaned membrane and

of a virgin membrane. The flux as a function of time (the so-called flux profile) is also a good measure of the occurrence of pollution. After all, if no pollution occurs, it will be constant, while the flux will decrease in the case of pollution. In this investigation, the same module has always been used (unless otherwise stated) because the history of use of a membrane is extremely important. If necessary, in the case of an incomplete cleaning, a treatment can be carried out with the TEMPO system and, as will appear below, this will return the performance of said membranes to virgin level. The same surface water (Twente canal water) has also been employed as much as possible. In those cases in which there has been a deviation from this, this is stated.

*Embodiment 1: Flux profile of a membrane using clean water and surface water*

The membrane is placed in the TRX and, unless otherwise stated, filtering is carried out under cross-flow conditions. The permeate flux is measured as a function of time. Some cases have been limited to the measurement of the initial clean-water flux (SWF).

*Embodiment 2: Cleaning effect of various calcium binders (EDTA, polyacrylate, STPP and citric acid)*

The polluted membrane is placed in a solution of a calcium-binding substance. Its concentration is 10 grams/litre. The membrane is regularly agitated in the solution for one hour. The following substances have been tested: EDTA, polyacrylate, sodium tripolyphosphate and citric acid. The pH of said solutions is 9-11.

*Embodiment 3: Cleaning effect of dicarboxyinulin (DCI) and other calcium-sequestering (oxidised) polysaccharides*

The polluted membrane is placed in a solution of 0.5 g/l DCI (pH 9-11). The membrane is regularly agitated in the solution for one hour.

*Embodiment 4: Cleaning effect of hypochlorite/bromide/TEMPO*

A solution of 35 mg of TEMPO, 65 mg of NaBr and 2 grams of HOCl in 1 litre demineralised water is brought to a pH of 9-11 with the aid of acetic acid. The

membrane to be cleaned is placed in said solution for half an hour. During the reaction, the pH is kept constant by adding NaOH (2M). The membrane is regularly moved back and forth in the solution. The course of the reaction can be followed on the basis of both the hydroxide and the hypochlorite consumption.

5     *Embodiment 5: Cleaning effect of hypochlorite/bromide*

The procedure is identical to the above experiment (4), but no TEMPO is used.

*Embodiment 6: Simultaneous cleaning effect of DCI and hypochlorite/bromide*

The method is identical to (7); however, no TEMPO and bromide are added (pH range 8.5–11.5).

10     *Embodiment 7: Simultaneous cleaning with DCI and hypochlorite/bromide/TEMPO*

The polluted membrane is placed in a solution of approximately 2 g of HOCl, 35 mg of TEMPO, 65 mg of bromide and 500 mg of DCI (pH range 9–11). Tricarboxyinulin forms under the influence of the TEMPO system. This material will bind calcium ions to a greater extent so that the calcium-binding capacity will gradually increase.

15     *Embodiment 8: Cleaning effect of DCI in combination with hydrogen peroxide/DCI and manganese catalyst*

0.5 g of DCI is dissolved in 1 litre of water, after which hydrogen peroxide is added up to a concentration of 2 g/l, followed by 200 µg of an Mn complex (prepared from manganese sulphate and 2,4,9-trimethyltriazacyclononane. After the pH has been brought to 8, the polluted membrane is placed in the solution for half an hour, the membrane being regularly agitated in the solution.

*Exemplary Embodiment 9: Use of DCI and zeolite as calcium-ion binder*

The polluted membrane is placed for half an hour in a solution of DCI (0.5 g/l) at a pH of 12. The extent to which DCI binds calcium ions is investigated with the aid of a Ca ion selective electrode. Zeolite is added to the remaining solution so that the calcium ions present in the solution or those bound to DCI are transferred to the zeolite. This experiment is repeated a number of times to demonstrate that the

capacity for calcium binding is determined by the zeolite present. After each calcium-ion complexing step, the membrane is treated with the TEMPO system.

## Results

### *1.0 Characteristics of a virgin membrane (procedure 1)*

5 The initial clean-water flux (SWF) if demineralised water is used in the virgin membrane is  $1260 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ .

The flux profile (dead-end) in the case of permeation with Twente canal water is as follows:

	Time (min)	Flux ( $\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ )
10	0	960
	5	480
	10	312
	15	288
	20	228
15	25	222
	35	186

### *2.0 Cleaning of a polluted membrane (type 615724) with the aid, in sequence, of citric acid followed by cleaning with TEMPO (procedures 2 and 4)*

20 The cleaning of the polluted membrane with the aid, in sequence, of citric acid and the TEMPO system gave the following results:

SWF (citric acid)  $780 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  (appreciably lower than the original flux),

SWF (TEMPO)  $1080 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  (also lower than the original flux).

Treatment with citric acid followed by the TEMPO system gives only a partial cleaning and is therefore insufficient.

### *2.1 Cleaning of an incompletely cleaned membrane (2.0) with the aid, in sequence, of DCI and TEMPO (procedures 3 and 4)*

25 After treatment, in sequence, with DCI and the TEMPO system, the SWF is  $1260 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ . The membrane module is cleaned to virgin level with this system.



*3.0 Cleaning of the membrane 7A5471, polluted with Twente canal water and cleaned in sequence with polyacrylate and TEMPO (procedures 2 and 3)*

Note: In this experiment use has been made of another membrane.

The SWF (virgin) of this membrane is  $1530 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ . The SWF (after cleaning, in sequence, with polyacrylate and the TEMPO system) was  $840 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ . Complete cleaning is not achieved.

*3.1 Cleaning of the membrane incompletely cleaned under 3.0 with, in sequence, EDTA and TEMPO (procedures 2 and 4)*

After cleaning, in sequence, with EDTA and TEMPO, the SWF is  $1530 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ .

It is clear that complete cleaning to virgin level is now achieved.

*4.0 Cleaning of a polluted membrane with the aid of HOCl/bromide (procedure 5)*

The SWF of the virgin membrane is  $1260 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ , while it is  $1020 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  after cleaning with HOCl/Br<sup>-</sup>. Complete cleaning is not achieved with this system.

The SWF after cleaning, in sequence, with DCI and TEMPO is  $1260 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  (according to procedures 3 and 4). The membrane has been cleaned to virgin level with this system. The flux profile (dead-end) for permeation with Twente canal water is as follows (procedure 1):

Time (min)	Flux ( $\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ )
0	1260
25	210

The flux profile after cleaning is virtually identical to that of a virgin membrane (see 1.0).

*5.0 Simultaneous cleaning of the membrane with hydrogen peroxide and DCI*

After pollution according to exemplary embodiment 1, the membrane has been treated with hydrogen peroxide and DCI (procedure 8). After this treatment, the SWF is  $1260 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ , from which it is evident that complete cleaning has been achieved. After cleaning with DCI alone, the SWF is  $1170 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  and after treatment with peroxide alone, it is  $700 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ . N.B. The treatment with peroxide alone has been carried out on another virgin membrane, whose SWF was  $1530 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ .

*6.0 Cleaning of the virgin membrane 7A5471 with DCI followed by TEMPO (procedures 3 and 4)*

The flux profile (dead-end) for permeation with Twente canal water using another type of membrane is as follows (procedure 1):

5	Time (min)	Flux ( $\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ )
	0	960
	5	456
	10	294
	15	240
10	20	240
	25	210
	35	180

*6.1 Cleaning of membrane polluted under 6.0 with DCI followed by the TEMPO system (procedures 3 and 4)*

15 For treatment, in sequence, with DCI and the TEMPO system, the SWF was  $1530 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  and is identical to that of a virgin membrane.

*6.2 Cleaning with the TEMPO system followed by DCI (procedures 4 and 3)*

If oxidation and calcium binding are used consecutively, the SWF is also  $1530 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ . It can be concluded that the sequence in which these two important cleaning  
20 steps are carried out yields no differences.

*7.0 Simultaneous cleaning of the membrane 665724 after dead-end pollution with Twente canal water with a solution of hypochlorite and DCI (procedure 6)*

The SWF of the virgin membrane was  $1260 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ . After pollution with Twente canal water and after cleaning with HOCl and DCI, it was  $340 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ . In the case  
25 of this system, cleaning is therefore far from complete.

After this membrane had been cleaned with the combined DCI/TEMPO system (procedure 7), the SWF was  $1260 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ , which means that the membrane has now in fact been completely cleaned.

**8.0 Filtration with untreated and prefiltered (G2) Twente canal water**

The flux profile (dead-end) for permeation with untreated (i.e. unfiltered) Twente canal water is as follows (procedure 1):

	Time (min)	Flux ( $\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ )
5	0	1020
	2	660
	5	420
	10	300
	15	240

**8.1 Cleaning, in sequence, with EDTA and the TEMPO system (procedures 2 and 4)**

SWF (virgin)  $1530 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$

SWF (after cleaning with EDTA and then TEMPO)  $1530 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$

The membrane polluted according to 8.0 was cleaned to virgin level. The membrane was then polluted with prefiltered Twente canal water (G2) according to the flux profile below (procedure 1):

	Time (min)	Flux ( $\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ )
15	0	1020
	5	420

With Twente canal water there is no difference in flux profile between untreated and prefiltered canal water.

**9.0 Cleaning of the membrane 6I5724 polluted with Beatrix canal water**

The flux profile (dead-end) for permeation with Beatrix canal water is as follows (procedure 1):

	Time (min)	Flux ( $\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ )
25	0	1140
	5	696
	10	510
	16	420
	25	390

This profile therefore differs somewhat from that of Twente canal water. The SWF of the virgin membrane was  $1260 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  and after cleaning with the TEMPO system it was  $1260 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ . This membrane, polluted by filtration of Beatrix canal water, has also to be cleaned to virgin level using the DCI/TEMPO system (procedures 3 and 4).

*9.1 The flux profile (dead-end) for permeation with Beatrix canal water of the cleaned membrane is as follows (procedure 1):*

Time (min)	Flux ( $\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ )
0	1620
5	900
15	600
22	510

*10.0 Cleaning of a polluted membrane module with re-use of DCI and TEMPO reaction liquid (procedures 3 and 4)*

A membrane was polluted 5 times consecutively with Twente canal water and cleaned with the TEMPO system, use being made of the same solutions (dicarboxyinulin and TEMPO/NaBr, respectively). If necessary, a suitable material (DCI or hypochlorite, respectively) was added to the solution to maintain the capacity. The results are summarised in Table 1.

Table 1

Run	SWF ( $\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ )	Note
1	1500	
2	1450	
3	1080	HOCl appeared to be consumed. HOCl was topped up to 2000 ppm
4	1450	
5	1450	

The same experiment was carried out under the same conditions, but zeolite (1 g/l) was added to the DCI solution in order to bind the calcium bound to the DCI by means of ion exchange (procedure 9) (see Table 2).

Table 2.

Time <sup>a</sup>	F(1) <sup>b</sup>	F(2)	F(3)	F(4)	F(5)	F(6)	F(7)	F(8)
0	1440	1410	1440	1440	1395	1410	1440	1395
2	1080	1080	1050	1050	1050	1020	1080	1080
5	780		735	720		660	600	600
10	585	570	570	570	570	490	500	540
25	255	255	255	255	255	255	255	255

a. Time in minutes

b. F(1-8) = flux profile after cleaning (in  $\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ )

The calcium-ion concentration in the DCI solution was much lower than  $10^{-8}$  M. During the cleaning steps, it is seen that this increases to approximately  $10^{-6}$  M. However, treatment with zeolite causes the  $C_{\text{Ca}}$  to drop again to  $< 10^{-7}$  M.

The membrane was cleaned for half an hour with the same solution of DCI (0.5 g/l). The initial concentration was  $< 10^{-10}$  M Ca. After cleaning, the calcium-ion concentration was approximately  $10^{-8}$  M. The calcium-ion concentration (approximately  $10^{-8}$  M) had increased after treatment to approximately  $10^{-7}$  M. After treatment with zeolite, the  $C_{\text{Ca}}$  decreased to  $10^{-8}$  M. Treatment with the same solution of DCI (0.5 g/l) for half an hour caused the calcium-ion concentration to increase again to  $10^{-7}$  M. The calcium-ion concentration increased to  $10^{-6}$  M, but it had decreased again to  $10^{-8}$  M after treatment with zeolite.

### CLAIMS

1. A process of cleaning filters for water purification, characterised in that the filter is treated with a calcium-binding agent.
2. A process according to Claim 1, characterised in that the filter is also subjected to catalytic oxidation.
3. A process according to Claim 2, wherein the catalytic oxidation is carried out by treatment with hypochlorite in the presence of a di-tertiary nitroxyl compound.
4. A process according to Claim 3, wherein the di-tertiary nitroxyl compound is 2,2,6,6-tetramethylpiperidine-N-oxyl.
5. A process according to Claim 2, wherein the catalytic oxidation is carried out by treatment with hydrogen peroxide in the presence of a complex of a transition metal with a cyclic polyamine.
6. A process according to one of Claims 1-5, wherein the calcium-binding agent is a dicarboxypolysaccharide, a phosphate such as tripolyphosphate or a polyacetylamine, such as EDTA or NTA.
7. A process according to Claim 6, wherein the dicarboxypolysaccharide is dicarboxyinulin.
8. A process according to one of Claims 1-7, wherein a zeolite is also used.
9. A process according to Claim 8, wherein the filter is a plastic membrane filter, in particular, a polysulphone or polyether sulphone membrane.
10. A process according to one of Claims 1-9, wherein the filters are filters for the cleaning of surface water.

# INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/NL 98/00544

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B01D41/00 B01D65/06

According to International Patent Classification(IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 496 470 A (A. G. KAPLOFF ET AL.) 29 January 1985 see the whole document	1,6,10
X	US 4 740 308 A (H. A. FREMONT ET AL.) 26 April 1988 see column 4, line 7-12	1,6,10
A	see the whole document	2
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A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 452 (C-1099), 19 August 1993 & JP 05 103958 A (ATAKA KOGYO KK), 27 April 1993 see abstract	1,2
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Date of the actual completion of the international search

3 November 1998

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 98/00544

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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